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August 21, 1986

Ms. Roberta Wedge
Dynamac Corporation
1140 Rockville Pike
Rockville, Maryland 20852

Dear Ms. Wedge,

Enclosed is additional information CMA has received concerning the chemical disposition of 6-PPD and 7-PPD in tires.

While this information was not available for your meeting with the ITC it may still be helpful.

If you have any further questions, or if I can be of any assistance, please feel free to contact me at 887-1314.

Sincerely,

Kathryn A. Rosica
Manager
Rubber Additives Panel

WATER LEACHING OF ANTIOZONANTS

E. J. Latos and A. K. Sparks

Universal Oil Products Co., Des Plaines, Illinois

Since tyre performance can be markedly affected by environmental factors which are not incorporated in laboratory evaluation tests, a study has been made to evaluate several factors which effect the retention of antiozonants in rubber stock. p-Phenylenediamine antiozonants are extracted from both nr and sbr stocks by water, as shown by chemical analysis and decreased ozone resistance, with the losses increasing as the pH of the water is decreased. In general, at equivalent molecular weights, the symmetrical N,N'-dialkyl-p-phenylenediamines are extracted more easily than N alkyl, N'-phenyl-p-phenylenediamines. However, IPPD showed a greater loss than any other antiozonant commercially available. The amount of antiozonant extracted decreased with increasing molecular weight, with very little loss occurring with unsymmetrical p-phenylenediamines above molecular weight of 300 and symmetrical analogues above molecular weight 330. Ozone ageing of the the rubber stocks before extraction does not alter the extent of antiozonant loss.
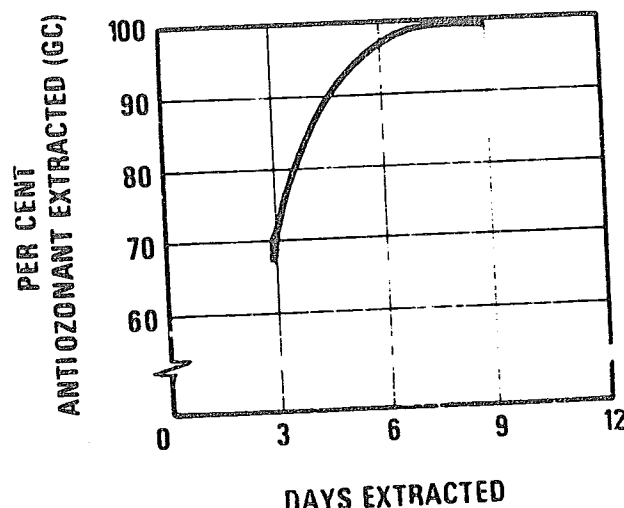
Fig. 1. Effect of time of leaching on percentage of DISP extracted from nr stock with tap water

PARAPHENYLENEDIAMINE antiozonants are used extensively in rubber products to inhibit degradation by ozone. Approximately 40 mlb. of antiozonant are used each year. These paraphenylenediamines are used primarily in vulcanisates based on unsaturated polymers.[1]

To make effective use of the paraphenylenediamine antiozonants, considerable effort has been made to characterise the behaviour and limitations of these compounds. Cox[2] has evaluated the effect of structure and concluded that the symmetrical N,N' - dialkylparaphenylenediamines are more active than the N alkyl, N'-aryl or N,N'-diarylparaphenylenediamines, although it is claimed that the N alkyl, N'-aryl compounds have antiflex cracking activity.[3]

Limitations of the paraphenylenediamine antiozonants have also been investigated. Lorenz[4] has shown that these antiozonants in vulcanisates are consumed during ozonisation and there is an apparent loss of antiozonant activity during shelf storage.[5,6,7] Spacht[8] has shown that with certain paraphenylenediamines, volatility during storage could result in a loss of antiozonant activity.

Despite these limitations, industry has found paraphenylenediamine antiozonants to be uniquely effective. Recently, however, another possible limitation to the use of these compounds has been reported.[9] It was shown that certain antiozonants, such as N isopropyl, N'-phenylparaphenylenediamine (IPPD), are leached from sbr and nr stocks by distilled water with a permanent loss of antiozonant activity. Loss of paraphenylenediamine antiozonants by water extraction could be of significant importance. It is the objective of this paper to report on the effect of molecular weight and structure of the paraphenylenediamine antiozonants and various water leachants on the extractability of these compounds from nr and sbr stocks.

Table 2
Molecular weight and structure of paraphenylenediamine antiozonants

Antiozonant	Molecular weight	Structure

DISP — 192

CH$_3$—CH—NH—⟨O⟩—NH—CH—CH$_3$ (with CH$_3$ groups)

N, N'-di-isopropyl-p-phenylenediamine

DCH — 272

⟨S⟩—N(H)—⟨O⟩—N(H)—⟨S⟩

N, N'-di-cyclohexyl-p-phenylenediamine

DMP — 304

CH$_3$—CH—CH$_2$—CH$_2$—CH—NH—⟨O⟩—NH—CH—CH$_2$—CH$_2$—CH—CH$_3$ (with CH$_3$ groups)

N, N'-bis(1, 4-dimethylpentyl)-p-phenylenediamine

DEMP — 332

CH$_3$—CH$_2$—CH—CH$_2$—CH—NH—⟨O⟩—NH—CH—CH$_2$—CH—CH$_2$—CH$_3$ (with CH$_3$, CH$_2$, CH$_3$ groups)

N, N'-bis(1-ethyl, 3-methylpentyl)-p-phenylenediamine

DMH — 332

CH$_3$—(CH$_2$)$_5$—CH—NH—⟨O⟩—NH—CH—(CH$_2$)$_5$—CH$_3$ (with CH$_3$ groups)

N, N'-di(1-methylheptyl)-p-phenylenediamine

DMO — 360

CH$_3$—(CH$_2$)$_n$—CH—N(H)—⟨O⟩—N(H)—CH—(CH$_2$)$_n$—CH$_3$ (with CH$_3$ groups)

N, N'-di(1-methyloctyl)-p-phenylenediamine

DTD — 472

CH$_3$—(CH$_2$)$_{10}$—CH—N(H)—⟨O⟩—N(H)—CH—(CH$_2$)$_{10}$—CH$_3$ (with CH$_3$ groups)

N, N'-di(2-tridecyl)-p-phenylenediamine

IPPD — 226

CH$_3$—CH—NH—⟨O⟩—N(H)—⟨O⟩ (with CH$_3$ group)

N-isopropyl-N'-phenyl-p-phenylenediamine

MBPD — 268

CH$_3$—CH—CH$_2$—CH—NH—⟨O⟩—N(H)—⟨O⟩ (with CH$_3$, CH$_3$ groups)

N-(1, 3-dimethylbutyl) N'-phenyl-p-phenylenediamine

MHPD — 296

CH$_3$—(CH$_2$)$_5$—CH—N(H)—⟨O⟩—N(H)—⟨O⟩ (with CH$_3$ group)

N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine

Note: **O** in a benzene ring denotes unsaturation **S** denotes saturation

into the sbr rubber stock, vulcanised and evaluated for antiozonant activity before and after extraction with the buffer solution. These data are sum- marised in Table 3. For the stock containing DISP, GC data indicate there should be a complete loss of antiozonant activity whereas the com- bined nitrogen data show a large but substantially lower degree of extrac- tion. The antiozonant activity data, however, correlate with the combined nitrogen rather than the GC analyses. DMH, a higher molecular weight PPDA, is not extracted, and there is no loss of antiozonant when evaluated with the GC, combined nitrogen content or antiozonant ac- tivity analyses.

The differences in behaviour of the N,N'-dialkyl- and N alkyl, N'- aryl.paraphenylenediamines in neutral and in acid solution are not difficult to explain if one considers the pro- cesses which may take place during the extraction procedure. The con trolling factor in neutral media is the rate of diffusion of the antiozonant out of the rubber stock, which is affected by the solubility of the dia- mine in the extracting medium and the size of the molecule being extracted. For a given molecular weight, the solubility and molecular size are approximately the same for both the symmetrical and unsymmetrical com- pounds, and accordingly one would expect little difference between the two types. As molecular weight increases, both decreased solubility and increased size reduce the ease of extractability.

In acid solution, however, one would expect salt formation to occur within the rubber matrix, and since the symmetrical para-phenylenedia- mines are more basic than the un- symmetrical analogues, at equilibrium a greater fraction of the dialkyl compounds should be present in the stock as the amine salt. Since these salts are quite water-soluble vis-a-vis the free amine, the symmetrical antiozonants should be more sus- ceptible to extraction by an acid solution than the unsymmetrical de- rivatives.

We have also shown that these salts do have antiozonant activity, although they cannot be determined quantitatively by GC analysis. There- fore, changes in the nitrogen content after extraction reflect losses of anti- ozonant by extraction whereas changes measured by GC analyses reflect both losses of antiozonant by extraction and also, qualitatively, conversion to the amine salt within the rubber matrix. Thus, the total nitrogen analyses correlate with the ozone resistance of the extracted stocks.

The leaching of antiozonant by water could have a significant in- fluence on the apparent useful life of an antiozonant in a rubber stock exposed to rain or melted snow. In table 4 is listed the pH for meteoric
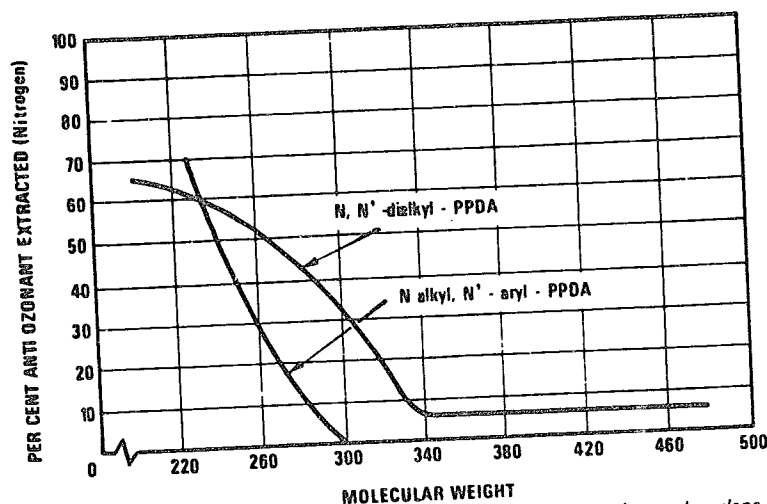
Fig. 6. Effect of molecular weight and structure on extractability of paraphenylene- diamine antiozonants with buffer solution (ph = 4·90) from nr stock
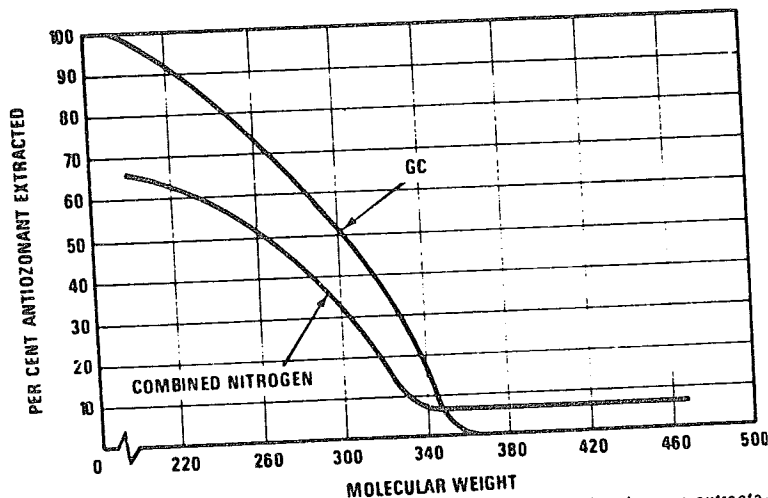
Fig. 7. Effect of molecular weight of N,N'-dialkylparaphenylenediamines on extracta- bility with buffer solution—comparison of gas chromatography and combined nitrogen data

Table 3

Antiozonant activity of sbr stock containing Disp or DMH after extraction for nine days with buffer solution (ph 4 90)

	% Antiozonant extracted, based on		Hours to first crack at 20% elongation in 50pphm ozone and 100 F	
Antiozonant	GC	combined Nitrogen	Original	After extraction
None	None	None	0–1	0–1
DISP	100	40 4	>168	8–24*
DMH	3 7	3 1	>168	>168

*Three large cracks only

Loss of Antioxidants in Truck Tyres
Part 1: Loss of Antioxidants during Mixing*

S. N. Chakravarty and S. K. Mustafi, Meerut (U.P., India) and R. R. Pandit, P. Sridharan and P. K. Pansare, Bombay (Maharashtra, India)

1. Introduction

The advantages of using antioxidants for protection of rubber vulcanizates became known in 1925. Use of secondary amines like PBN, DPPD, diphenylamine and its derivates and aniline-acetone condensates soon became common in the rubber industry. Then in sicentific fields, investigations were also started to find out the fate of the antioxidants in the rubber processing operations and in the rubber vulcanizate during service conditions.

D. Craig [1] found only a fractional recovery of amine antioxidant from unaged vulcanizates by acetone extraction; at one percent loading of the antioxidant, the vulcanizate retaining about half of the antioxidant. To explain the retention of the antioxidant in unaged vulcanizates, he suggested that active degradation sites along the molecule of rubber had reacted with the secondary amine. Later he [2] had found that the antioxidant could be extracted from the vulcanizate to a greater extent by steam distillation of powdered vulcanizate previously refluxed few hours with sodium hydroxide solution. This observation however became completely neglected till date. Due to the unsolved riddle of partial recovery of antioxidants from unaged vulcanizates in their work on antioxidants in rubber vulcanizates, Lorenz and Parks [3], Tsurugi and Murakami [4], started adding antioxidants to rubber vulcanizates by imbibing antioxidants into rubber vulcanizates from solutions of the antioxidants in rubber swelling solvents, rather than adding antioxidants to the rubber compound before vulcanization. However, when both the teams tried to follow the antioxidant consumption during the ageing of the vulcanizates, they came across the surprising fact that antioxidant protection continued in the vulcanizate long after the time the solvent extractable content of antioxidant in the vulcanizate had dropped to zero.

As recently as in 1979, Shcherrba et al. [5] studied "The consumption of antioxidants under various vulcanizing conditions". They found that phenolic antioxidants are not consumed but amine antioxidants were consumed. They attributed the loss to reaction of antioxidant with vulcanizing agent, absorption by the filler and reaction with oxygen absorbed on the filler.

We thought it to be probable that during processing of rubber compounds, amine type antioxidants are becoming partially nonextractable by normal solvent extraction procedures and this solvent nonextractable antioxidant has still the capacity to give antioxidant protection to the rubber vulcanizate in Lorenz and Parks and Tsurugi's investigations.

Antioxidants are petrochemical based and with the increasing prices of crude oil, the prices of antioxidants are going up. It is essential to rationalize the usage of antioxidant and to avoid any loss of antioxidant during processing. Chakravarty and Pandit [6] had shown that antioxidants retard the peptisation of NR by activated pentachlorothiophenol (Renacit 7). These results had indicated the possibility that during the mixing of NR compounds, antioxidants may be getting consumed while they are retarding the breakdown of NR – an oxidative degradation process.

Reztsova et al. [7] had shown that if antioxidant is masticated with NR for a longer time, the fatigue life of the vulcanizate becomes less. These results also indicate probable consumption of antioxidant during mixing process.

The aim of the present investigations was therefore to find out a) at what stage during processing of rubber, the amine antioxidants become partially nonextractable by solvents, b) the reasons for the nonextractability and c) an extraction procedure so that the amine antioxidants can be extracted as completely as possible and then estimated quantitatively. Further aim was to use the extraction method to estimate the loss of antioxidants during mixing operations.

2. Experimental

All investigations were carried out using the antioxidant IPPD.

2.1 Antioxidant Extraction Procedure

For uncured compounds, standard acetone extraction procedure (IS 3660 – Part II: 1968) was followed. For vulcanizates, the extraction procedures developed are given in text.

2.2 Antioxidant Estimation Method

The antioxidant was estimated by the procedure developed by Ostromow [8] after slight modification. In this method, the antioxidant is coupled with Nitrazol CF extra (p-nitrobenzene-diazonium fluoroborate) to give a colour solution. The absorbance of this solution at 376 nm was measured using spectrophotometer model 106 (Mark II) manufactured by M/s. Systronics, Ahmedabad.

The Ostromow procedure had to be slightly modified. At room temperatures in Bombay (ca. 30°C), the colour formed was found to be rather unstable. Hence after addition of solution of Nitrazol CF extra, the measuring flasks were transferred to an icebath kept in a refrigerator. The colour development, however, took a longer time (Figure 1). A time of 2 h was found to be adequate for full development of colour. The flasks were allowed to warm up in ambient temperature to temperature above dewpoint of ambient air before measurements were made to avoid condensation of moisture on the measuring cell.

3.2 Extraction of antioxidant from vulcanizates

Efficiency of extraction of antioxidant from the vulcanizate was found to depend on the particle size of the crushed vulcanizate sample. Grinding of the vulcanizate on the laboratory mill was found to make the vulcanizate samples very hot. There was then a likelyhood of oxidative degradation and consequent loss of antioxidant. A small hand driven two roll mill (rolls 24 x 53 mm and 45 x 53 mm) with a friction ratio of about 1 : 1,9 was designed. The small diameter roll was grooved. With this handmill, it was possible to grind the vulcanizate finely without development of much heat.

Standard acetone extraction procedure lasting for 16 h is rather inconvenient to use due to the long extraction period involved. *Baker et al.* [9] had recommended direct refluxing of vulcanizate in a mixture of toluene + methanol as a faster extraction procedure. As a solvent medium a mixture of 32 vol toluene + 92 vol methanol was selected since it has a boiling point very near to that of acetone.

To judge the efficacy of the two extraction procedures, experiments were carried out with samples of the same vulcanizate (1D) as given in *Table 3*.

Table 3. Comparison of extraction procedures

A	B
Standard acetone extraction of vulcanizate 16 h extract rejected	Vulcanizate refluxed with toluene methanol mixture 2,5 h extract rejected
↓	↓
Residue washed with acetone	Residue washed with acetone
↓	↓
Residue refluxed with toluene methanol mixture 2,5 h	Standard acetone extraction of the residue 16 h
↓	↓
Extract A tested by thinlayer chromatography	Extract B tested by thinlayer chromatography
↓	↓
IPPD present	IPPD absent

Extract A showed the presence of IPPD but not extract B. It was evident that the 2,5 h direct refluxing of the vulcanizate with toluene methanol mixture was a more efficient extraction procedure for antioxidant extraction than the 16 h soxhlet extraction with acetone.

However, even two extractions by refluxing with toluene-methanol mixture each extraction lasting for 2,5 h failed to extract the antioxidant completely. The antioxidant extracted from vulcanizate 1D was 1,51 phr in place of 2,5 phr originally added in the compound. It was evident that the zinc-IPPD complex was not getting extracted.

Craig [2] had used aqueous sodium hydroxide solutions. However, in place of the prolonged extraction given by him, we decided to evaluate ammonia instead. So addition of ammonia to toluene methanol mixture was then tried with the anticipation that the ammonia will displace IPPD from zinc-IPPD complex. The results were still disappointing. It was observed that zinc was also getting extracted as zinc ammonia complex. When the extracts were made free from solvent, the zinc ammonia complex decomposed expelling ammonia and reforming zinc-IPPD complex. This difficulty was then overcome by addition of aqueous solution of sodium salt of ethylenediamine tetracetic acid. The results were encouraging.

However, when this procedure was being evaluated in NR based tyre tread type compound the swelling of the vulcanizate in toluene methanol mixture was found to be inadequate. Hence, one more extraction step was introduced using toluene as the swelling medium. Liquor ammonia is not soluble in toluene and hence in place of liquor ammonia diethylamine which is soluble in toluene was used. The procedure which was found to be adequate for both gum and filled NR vulcanizates is given in details in *Table 4*. The table also gives the IPPD content of the vulcanizates 1D, 2D, 3D and 4D obtained using this procedure.

Table 4. Procedure for antioxidant extraction from NR vulcanizates

i) 3 gm vulcanizate powdered on a 2 roll handmill.
↓
ii) Addition of 50 ml toluene + 2 ml diethylamine soaked overnight and decanted (extract 1).
↓
iii) Residue twice extracted under reflux each time using 50 ml mixture of (toluene + methanol) (32 vol + 92 vol) + 2 ml diethylamine and refluxing 2,5 h, over waterbath (extracts 2 and 3).
↓
iv) Residue washed twice each time with 10 ml (toluene + methanol) residue discarded (washings).
↓
v) Extracts 1 + 2 + 3 + washings + 10 ml aq. $\frac{1}{5}$NaEDTA solution.
↓
vi) Solvent distilled off over waterbath to dryness. Last traces of solvent removed in a current of oxygenfree nitrogen.
↓
vii) Dry residue + 2 drops of aq. $BaCl_2$ solution 20 % + 2 drops 4 N ammonia + 10 ml methanol[a]. Wholemass cooled to 10°C in refrigerator.
↓
viii) Supernatant liquid + 3 washings of the residue each time with 25 ml methanol.
Volume made to 100 ml – solution A.
↓
ix) 5 ml solution A diluted to 100 ml with Methanol[a] – solution B.
↓
x) 12 ml solution B + 4 ml 0,1 % freshly made aq. solution of nitrazol CF extra + 1 ml 1N HCl.
Volume made to 20 ml. Flask kept in crushed ice and transferred to refrigerator for 2 h.
↓
xi) Flask rewarmed till just above dew point at ambient air. Absorbance of the solution measured at 376 nm[x] (for IPPD) on spectrophotometer.
(x For other amine antioxidants the wavelength for peak absorption to be predetermined).
Antioxidant content checked from calibration curve predetermined using the antioxidant.

Vulcanizates	1D	2D	3D	4D
IPPD content phr	2,1	2,1	2,07	2,06

[a] Methanol = Spectroscopic grade Methanol

The procedure gives an efficiency of antioxidant extraction of about 90 – 95 %. The small loss is most likely to be mechanical in nature occurring in the last extraction of the antioxidant from the dry residue of solvent extract (step VIII Table 4). The volume of three extracts + washings is about 190 ml. When the solvent is dried off the small quantity (70 mg or less) of the antioxidant is spread over the large bottom area of the flask. Even the four washings with methanol may not be dissolving the antioxidant adhering tenaciously to the glasswall and the salt residue of sodium chloride + ZnEDTA + barium stearate.

The antioxidant masterbatch A had given antioxidant content of 2,21 phr. The vulcanizates 1D to 4D had given almost a consistent value 2,1 phr for the antioxidant content. The loss could have occurred during the further mixing process.

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Table 10. Trials made in production internal mixer Werner & Pfleiderer model GK 230

Set A		Set B		Set C	
IPPD addition in the carbon black masterbatch stage		IPPD addition to the carbon black masterbatch at remill stage		IPPD addition to the carbon black masterbatch at the final stage	
Mooney viscosities of final compounds – ML_4 at 100°C					
A_1	56	B_1	55	C_1	55
A_2	57	B_2	55	C_2	55
A_3	58	B_3	54	C_3	54
Average	57		55		55
IPPD content in the vulcanizate phr dosage of IPPD 2,0 phr					
A_1	1,64	B_1	1,82	C_1	2,05
A_2	1,90	B_2	1,80	C_2	1,87
A_3	1,76	B_3	1,80	C_3	1,97
Average	1,77		1,81		1,96

Thus all experiments indicate that in case of NR compounds, it is advantageous to add the antioxidant at the final stage. Addition of antioxidant at the remill stage is not as effective. The reason may be that the NR at this stage has a large number of hydroperoxide groups formed during the masterbatch stage. These hydroperoxide groups decompose during the remill stage. Some oxidative degradation also occurs during this stage. Both effects lead to some consumption of antioxidant. In the final on the other hand, when sulfur is added, perhaps a trace of sulfur dioxide is formed and all hydroperoxide groups are catalytically destroyed to nonradical groups. Antioxidant when added at this stage is not consumed.

The batch temperature during the final stage in internal mixer is of the order of 105 – 110°C. Antioxidants whose melting points are well below this temperature can melt and can get easily dispersed in the mass. With antioxidants whose melting points are higher than the above mentioned temperature range, it will be essential to use these antioxidants only in fine powder form to ensure their satisfactory dispersion in the rubber mass during the final stage.

Another advantage of addition of antioxidant in the final stage is the reduced viscosity and consequently better processibility of the compounds. It is no use achieving ultimate low viscosities of compounds by increasing the premastication. Then the carbon black dispersion becomes a problem with resultant loss in wear and tear properties and flex fatigue life. The mastication of NR occurs not only during the premastication stage but also during the mixing process till the sulfur is added. For better carbon black dispersion, it is preferable to achieve the viscosity degradation after incorporation of the carbon black. Addition of antioxidant at the final stage achieves these objects.

The customary addition of antioxidants at the beginning of mixing cycles entails a double loss. The processibility of the compounds is reduced due to the retarded mastication of the NR during the mixing stage. Valuable antioxidant is simply lost in this process without any benefit whatsoever. Antioxidants are added to rubber compounds with the sole purpose of improving the service life of the vulcanizate. It is therefore of paramount importance that the antioxidant retention at the end of the mixing is as high as possible.

4. Summary

The reason for incomplete extraction of antioxidant from vulcanizate by solvent has been shown to be due to formation of complex of the amine antioxidant with zinc oxide and its compounds formed inside rubber vulcanizate. The complex is insoluble in solvents. Hence the antioxidant does not get extracted completely by the solvents.

The zinc amine antioxidant complex can be broken down by using amines like diethylamine along with the solvent. Based on these findings, an extraction procedure has been devised.

In mixing of NR compounds, the antioxidants can get consumed to certain extent while preventing the oxidative breakdown of the NR. It is preferable to add antioxidant towards the end of mixing cycle along with the sulfur. The addition of antioxidant along with sulfur gives lower compound viscosity and better antioxidant retention.

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Table 3 Procedure for antioxidants extraction from NR vulcanizates

1) 3 g vulcanizate powdered on a 2 roll handmill
2) Addition of 50 ml toluene + 0,4 ml conc. HCl (30 %) AR
   Soaked overnight and decanted (extract 1)
3) Residue twice extracted under reflux each time using 50 ml mixture of (toluene + methanol) (32 vol. + 92 vol.) + 0,4 ml conc. HCl (30 %) and refluxing 2,5 h over waterbath (extracts 2 and 3)
4) Residue washed twice each time with 10 ml (toluene + methanol) Residue discarded (washings)
5) Extracts 1 +2 + 3 + washings + 10 ml aq. M/5 NaEDTA solution + few ml alc. KOH to make solution alkaline
6) Solvent distilled off over waterbath to dryness.
   Last traces of solvent removed in a current of oxygen free nitrogen.
7) Dry residue + 2 drops of aq. BaCl₂ solution 20 % + 2 drops 4 N ammonia + 10 ml methanol. Whole mass cooled to 10°C in refrigerator
8) Supernatant liquid + 3 washings of the residue each time with 25 ml methanol.
   Volume made to 100 ml (solution A)
9) 5 ml solution A diluted to 100 ml with methanol*(solution B)*
10) 12 ml solution B (quantity varied in case the absorbance was outside limits of 0,2 – 1,0) + 4 ml 0,1 % freshly made aqueous solution of nitrazol CF extra + 1 ml 1N HCl volume made to 25 ml. Flask kept in crushed ice and transferred to refrigerator for 2 h
11) Flask rewarmed till just above dewpoint of ambient air. Absorbance of the solution measured at specific wavelength for the antioxidant as given in table 4.
    Antioxidant content checked from calibration curve predetermined using the antioxidant.

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* methanol* – spectroscopic grade methanol

Table 4. Wavelength for peak absorbance and stability of the color

Antioxidant	IPPD	6PPD	DTPD	TMQ	ADPA HV	ADPA LV	PBN
Wavelength for peak absorbance nm	376	385	385	505	480	480	520
Time to develop full color at 0°C min	95	95	120	80	70	70	10
Maximum stability period of color min	210	210	280	135	135	135	135

2.3 Thermogravimetric analysis

Thermographs of the antioxidants were taken between 40°C and 200°C on Thermal Analysis system series 30 (Shimadzu Corpn., Japan) under constant flow of nitrogen at the rate of 30 ml/min and heating rate at 5°C/min.

2.4 Evaporation from petridishes

The loss in weight of 10 g of the antioxidant from 8 cm dia. petridishes at 100°C was measured.

2.5 Accelerated ageing test

Ageing of dumbell test pieces was carried out either at 100°C or 70°C in a Wallace Multicell Ageing oven with air rate at 7 volume changes per hour.

Ageing of blocks (100 mm x 100 mm x 28 mm) was carried out in a specially constructed multicell ageing oven. Excepting one surface (100 mm x 100 mm) rest of the five surfaces of the block were covered with aluminium foil using polychloroprene adhesive. Hot air passed alongside the exposed surface of the block at a velocity calculated to be approximately 7,5 m/h at air rate of 7 volume changes per hour.

After the ageing period 25 mm portion of four sides of the block was cut off. The central part was then sliced parallel to the exposed surface into six layers, top exposed layer 3 mm thick and the rest 5 mm thick. These were then used for estimation of antioxidant content and total nitrogen content.

2.6 Volatilisation due to air velocity

Blocks covered with aluminium foil as before on five sides were fitted onto a wooden board in a row. The board was mounted on top of the drivers cabin such that the exposed 100 mm x 100 mm surface faced the direction of travel. Two sets of blocks were exposed. One set was removed after 15000 km and the other after 28000 km run of the truck. The blocks were then analysed for antioxidant content and total nitrogen content as in the accelerated ageing tests above.

3. Results and discussions

3.1 Antioxidant extraction method and estimation method

In Part 1 of this paper, Chakravarty et al. had found that IPPD forms complex with zinc oxide or its compounds formed during mixing and vulcanization and that IPPD could be extracted using diethylamine alongwith the extracting solvents. This aminic solvent extraction method was found to give satisfactory results with IPPD, 6PPD, DTPD and PBN but it was found unsatisfactory with vulcanizates containing TMQ and ADPA types.

Tsurugi et al. [7] had tried use of very dilute aqueous solutions of hydrochloric acid for extraction of antioxidant from vulcanizate residue after solvent extraction. Hence instead of 2 ml diethylamine, addition of 0,4 ml concentrated hydrochloric acid (30 %) to the solvents toluene and toluene-methanol was tried. (The quantity of acid chosen was sufficient to react with all zinc oxide in the vulcanizate sample taken.) Since for precipation of zinc-EDTA complex at the final step required alkaline conditions, after addition of M/5 NaEDTA solution, the pH was brought up on alkaline side by addition of alcoholic KOH whenever necessary.

The spectrophotometric method using 4 nitrobenzene diazonium fluoroborate as coupling agent was found to be suitable for estimation of the following antioxidants: IPPD, 6PPD, DTPD, TMQ, ADPA-HV, ADPA-LV and PBN.

The stability of the colors developed was not found to be equal for all the antioxidants. The stability periods of the colors when the flasks are stored in crushed ice are shown in Table 4.

Hilton [8] had given for color development with diazotised 4 nitroaniline and amine antioxidants a period of 90 min at room temperature for all antioxidants excepting PBN. However storage period of 120 min in dark in crushed ice bath could be used for all the above antioxidants. For TMQ, ADPA-HV, ADPA-LV and PBN however, the absorbance measurements had to be completed within 15 – 20 min of removal from the crushed ice bath.

As also reported by Hilton [8] this method could not be used for the estimation of 77PD and ETDQ. ADPA resin was not soluble in methanol the solvent used for the estimation method. For estimation of 77PD the method developed by *Lorenz* and *Parks* [9], potentiometric titration with 0,1 N perchloric acid in non-aqueous medium was tried. To use this method for the extracted antioxidant, the methanolic extract was evaporated to dryness and the residue was redissolved in glacial acetic acid. The results were erratic perhaps due to contamination with EDTA.

Gas chromatographic method (GC) was tried. On Hewlett Packard Gas Chromatograph model No. 5730B equipped

3.4 Standard accelerated ageing tests

The normal criterion used for evaluations of antioxidants in a vulcanizate is the retention of physical properties of thin specimen of the vulcanizate after ageing at elevated temperatures. There is no doubt that the retention of physical properties should be the foremost criteria, since the very purpose of use of an antioxidant in a rubber vulcanizate is to preserve the physical properties of the vulcanizate over a long service life. The only factors to be checked in these accelerated ageing tests are the temperature selected and the duration of ageing, so that the results obtained from these tests will reflect the long range performance at the service temperature.

The traditional temperature of ageing of vulcanizates from tyre compounds is 100°C. The ageing period used varies from tyre company to tyre company and is 1 – 4 d.

The vulcanizates with the different antioxidants were therefore aged in a multicell ageing oven at 100°C for 1, 2 and 4 d. The criteria adopted for these NR based vulcanizates was the retention of tensile strength on ageing. *Figures 3 and 4* show the percent retention of tensile strength as a function of duration of ageing period.

The tensile strength retention characteristics with the different PPDs were almost identical within experimental error. The liquid antioxidant 77PD gave same retention upto 2 d ageing and only marginally less on 4 d ageing than the solid PPDs. In the heat resistant class the liquid ADPAs were giving as good protection as that given by the solid antioxidants TMQ and ADPA resin. The protection given by these four antioxidants was but only marginally less than that given by the PPDs. Only ETDQ and PBN gave significantly lower protection.
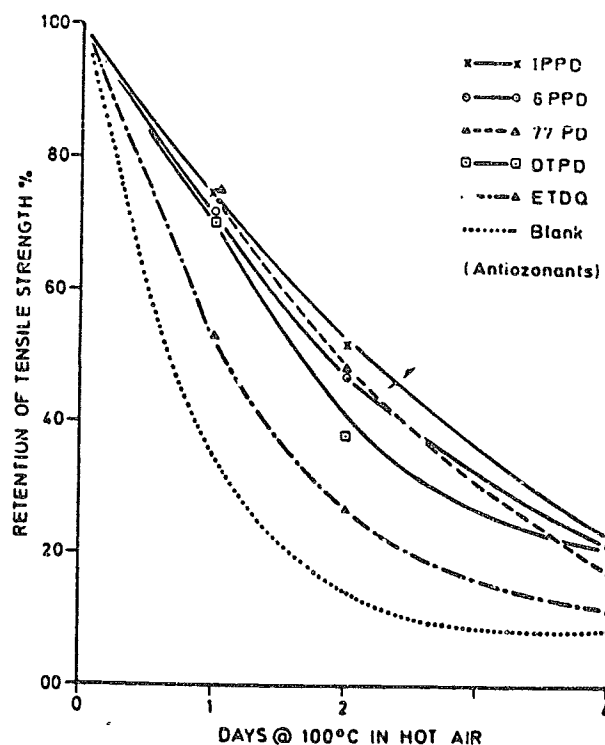

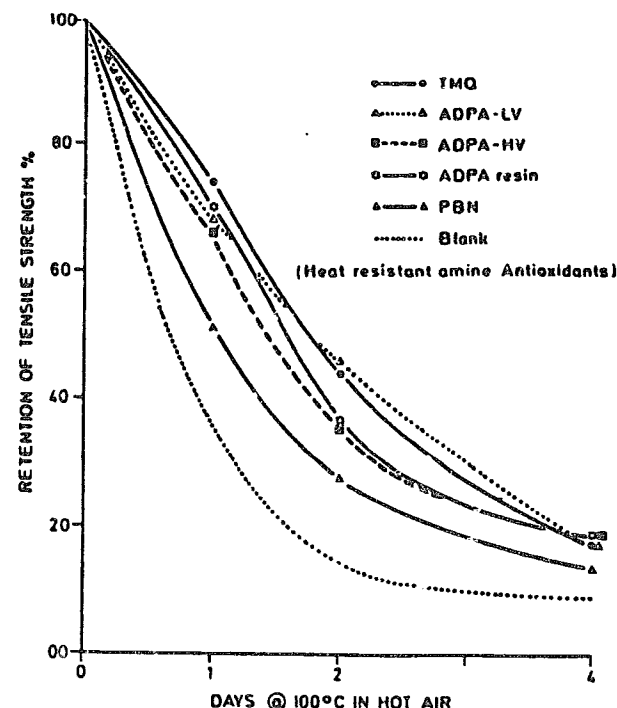Figure 3. Retention of tensile strength — NR tread type vulcanizate

Figure 4. Retention of tensile strength — NR tread type vulcanizate

An apparent conclusion from these results is that volatility of the antioxidant does not play any significant part in the ageing of vulcanizates at 100°C. This is also confirmed by the estimation of total nitrogen content of the vulcanizates.

The antioxidant residues left after donation of the hydrogen atom of the — NH-group either dimerise (A – A or A – A – H) or get bound to the polymer [11]. In both the cases the products are likely to be less volatile than the original antioxidant. Hence if any excess loss in nitrogen content of the vulcanizate (over that of control without antioxidant) occurs during ageing of the vulcanizates, the loss can be safely attributed to the loss of the antioxidant rather than to the loss of antioxidant reaction products. In case there is no volatile loss of the antioxidant the % total nitrogen content level in the vulcanizate should remain constant after ageing.

Table 6 shows the loss in the % total nitrogen content tested in some of the vulcanizates before and after ageing as also equivalent loss of antioxidant content based on nitrogen contents of the antioxidants used. The vulcanizates with the liquid antioxidants 77PD, ETDQ, ADPA-LV, ADPA-HV or the solid antioxidant TMQ are hardly showing any loss of antioxidant after ageing at 100°C for 4 d.

Table 6. Loss in % total nitrogen content — ageing of dumbells 4 d at 100°C (Original dosage of antioxidants 2,5 phr)

Antioxidant	77PD	ETDQ	ADPA HV	ADPA LV	TMQ
Loss in % total nitrogen	0,004	0,002	0,003	0,002	Nil
Equivalent loss in antioxidant content phr	0,07	0,085	0,045	0,085	Nil

In estimation of antioxidants from aged vulcanizate by spectroscopic method, there was a doubt that any ex-

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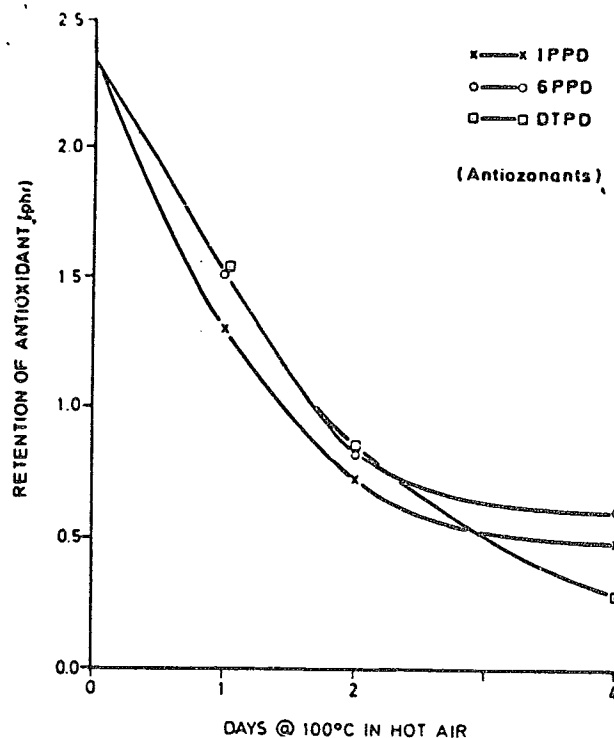Kautschuk + Gummi Kunststoffe 36 Jahrgang. Nr. 5/83

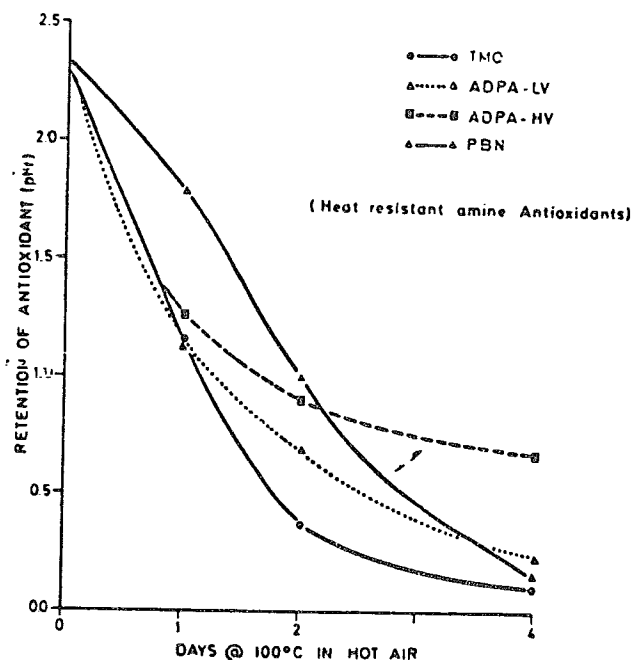Figure 6. Antioxidant retention in vulcanizates — NR tread type vulcanizate

Figure 7. Antioxidant retention in vulcanizates — NR tread type vulcanizate

carried out ageing of blocks of rubber vulcanizates at 150°C and found that most of the oxidation occured in the 0,25 mm layer on the surface and in the interior below 1 mm from the surface, oxidative degradation was negligible. In the interior regions degradation of the rubber vulcanizate occured solely due to anaerobic ageing (post vulcanisa-tion-reversion). <u>Antioxidants offer protection only against oxidative ageing — the type of ageing occuring predominantly on the surface of the thick article. Antioxidants are of no help in the anaerobic ageing occuring in the interior of the article. Hence when antioxidant protection is being designed for a thick rubber article like the truck tyre the ageing conditions prevalent near the surface have to be taken into account.</u>

As started earlier, the surface temperatures of truck tyre tread under service conditions in India are in the region of 70°C. Average life of an Indian truck tyre is about 60 000 km on the plains. Average running speed of the trucks is about 40 km/h giving a running life of 1500 h for the truck tyre. Taking the steadystate high temperature service life as approximately 80 % of the total running life, one can assume the truck tread surface to remain around 70°C for about 1 200 h of the high temperature working life expectancy of the crossply truck tyres in India.

With these facts in consideration, the ageing of the NR tyre tread type compounds was carried out at 70°C, for 1 week, 2 weeks, 4 weeks and 7 weeks (1 176 h).

Figures 8 and 9 show the retention of tensile strength on ageing at 70°C. IPPD gave the best retention followed by 6PPD and DTPD. Unlike during the ageing at 100°C the liquid 77PD gave good protection upto 2 weeks but then the protection fell off rapidly. Amongst the heat resistant class, the solid antioxidants TMQ and ADPA resin gave the best protection but far below that given by IPPD. The next in efficacy was PBN. The liquid antioxidants ADPA-HV and ADPA-LV gave the lowest protection.
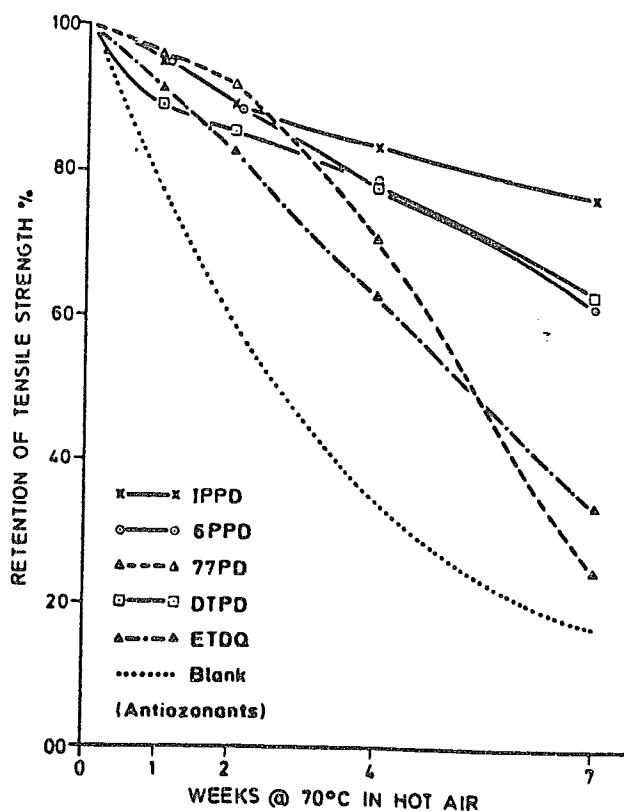

Figure 8. Retention of tensile strength — NR tread type vulcanizate

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Figures 11 and 12 show the retention of seven antioxidants in the vulcanizates after ageing. The PPD class gave lower antioxidant retentions, IPPD showing the least retention among PPD antioxidants. Amongst the heat resistant class, TMQ had shown the best retention while ADPA-LV showed the least retention. In these estimations only ADPA-LV showed some indication of volatile loss.

Table 7 shows the loss in % total nitrogen content for some of the vulcanizates after ageing. Here the vulcanizates containing liquid antioxidants showed a high loss in nitrogen content as compared to the vulcanizates containing solid antioxidants. This definitely indicates that under service temperature conditions of the tyre there is a considerable loss of liquid antioxidants due to volatilization.

Table 7. Loss in % total nitrogen content — ageing of dumbells 7 weeks at 70°C (Original dosage of antioxidants 2,5 phr)

Antioxidant	77PD	ETDQ	ADPA HV	DTPD	TMQ	ADPA resin	PBN
Loss in % total nitrogen content	0,021	0,026	0,024	0,001	0,001	0,005	0,007
Equivalent loss in antioxidant content phr	0,36	1,05	0,53	0,02	0,03	0.10	0,16

3.6 Comparison of ageing tests at 100°C and at 70°C

It is axiomatic that higher the test temperature higher should be the volatile loss of liquids. The antioxidants alone would follow this rule too. However in case of volatile loss of antioxidant from rubber vulcanizate the rate of volatilization, as shown by Kuzminskii [3] will also depend on the concentration of the antioxidant on the surface of the vulcanizate during ageing. At 100°C, the antioxidant depletion from the surface of NR based normal sulfur cure vulcanizates will be fast due to the following reasons:

a) High rate of oxidation. If the temperature coefficient of oxidation is taken as 2,77 per 10°C [16] the rate of oxidation at 100°C will be 21,25 times the rate of oxidation at 70°C.

b) Different stoichiometry of antioxidant consumption. At lower temperatures of oxidation when the hydroperoxides are comparatively stable, the antioxidant (AH) stops the free radical chain propagation as follows:

$$RO_2 \cdot + AH \rightarrow ROOH + A \cdot$$

i.e. one molecule of antioxidant is able to terminate one free radical chain.

The stability of the hydroperoxide is dependent on the temperature. *Cain* et al. [17] had shown that even at 75°C about 75 % of the hydroperoxides in aged NR gum vulcanizate decomposed in 24 h. Alkyl hydroperoxide like t-butyl hydroperoxide completely decomposes at 89°C. Ethyl hydroperoxide explodes if temperature goes above 100°C [18]. This means that at 100°C the hydroperoxides formed in NR vulcanizate will also decompose as soon as they are formed. Under these conditions the antioxidant (AH) can terminate the free radical chain only by converting the peroxy free radical ($RO_2 \cdot$) to stable non radical alcohol group ROH e.g.

$$RO_2 \cdot + 3AH \rightarrow ROH + H_2O + 3A \cdot$$

This means that three antioxidant molecules will be necessary to terminate a single free radical chain at 100°C.

c) Possibility of oxidation of the antioxidant itself. Lorenz [19] had shown that at 100°C PPD antioxidants do get oxidised in presence of oxygen.

Due to the above causes, it is most likely that at 100°C, the rate of antioxidant depletion at the surface of the vulcanizate will be very high. In consequence the concentration of antioxidant at the surface will be very low being entirely dependent on the rate of diffusion of the antioxidant from the interior to the surface. Hence the loss of the antioxidant due to volatilization during the ageing is negligible. Solid or liquid antioxidants can be expected to give almost comparable performance during ageing of NR based normal sulfur cure vulcanizates at 100°C. In case of EV or thiuram cure vulcanizates or synthetic rubber vulcanizates whose rate of oxidation is low at 100°C, the effect of volatility of liquid antioxidants will become evident even during ageing at 100°C. At 70°C due to the comparatively low rate of consumption of antioxidant, antioxidant is present on the surface in adequate concentration and volatility effects become more pronounced.

Even for comparative grading purposes also the short term ageing at 100°C can give very different results than the long term ageing at the service temperature of 70°C.

Ageing at 100°C (results after 2 d ageing) give the following grading for the antioxidants in order of decreasing performance:

IPPD > 77PD > 6PPD > ADPA-HV > TMQ > DTPD
ADPA resin > ADPA-LV > PBN > ETDQ > BLANK

Seven weeks ageing at 70°C gave the following grading:

IPPD > 6PPD ≈ DTPD > ADPA resin > TMQ > ETDQ
> PBN > ADPA-HV > 77PD > ADPA-LV > BLANK

Long term ageing tests at 70°C are far more time consuming than the short term ageing tests at 100°C. The long term laboratory ageing tests are however definitely less time consuming and less costly than the actual field evaluation of the experimental truck tyres.

Long term ageing tests are not uncommon. For automotive rubber goods, auto manufacturers like Daimler-Benz have started specifying in their purchase specifications for rubber goods, ageing tests at service temperature for a duration of 1000 h for car components and for duration of 3000 h for truck components [20].

3.7 Ageing of blocks

The dumbell type tensile strength test specimen are thin ca. 2 mm. The surface area per unit weight of the vulcanizate is very large and the antioxidant level gets depleted at a very fast rate. Truck tyres are comparatively thick. As the antioxidant is consumed at the surface, the antioxidant concentration at the surface is brought up by diffusion of antioxidant from interior to the surface. Hence it was decided to use 28 mm thick blocks. The interior regions of the running truck tyre tread may have a temperature of about 110 – 115°C but there is little or no oxygen reaching these regions. The temperature is around 70°C on the tread surface side exposed to oxygen. Such differential

As in case of blocks aged at 70°C, liquid antioxidants show considerable loss, 0,3 – 1,0 phr as compared to about 0,1 phr in case of solid antioxidants. The 28 mm thick blocks had an exposed area of 100 cm², a weight of 300 g and an antioxidant content of 4,5 g. Even 0,5 phr loss means a volatilization rate of 0,9 g/100 cm² area. A lug type tread of 900-20 size truck tyre has an exposed area of 9200 cm² and the same rate of volatilization would mean a loss of 82,8 g out of about 300 g used in tread compound.

The loss due to volatility is unfortunately difficult to measure on a truck tyre under service conditions. The migration of accelerators and antioxidants in the tyre, the presence of nylon cord body containing large quantities of nitrogen and the continuous wearing off of the tread surface containing the antioxidant residues make it difficult to get any nitrogen balance. Hence study on blocks mounted on trucks is a convenient method to study the loss of antioxidants due to volatilization.

4. Summary

An experimental procedure suitable for extraction of wide range of amine antioxidants from rubber vulcanizates has been developed.

It has been shown that the customary ageing test at 100°C for NR based tyre tread compounds does not reflect the loss of the antioxidant due to volatility, the probable reason being low concentration of the antioxidant on the surface of the vulcanizate due to the rapid rate of consumption. Long term ageing test at tyre surface temperatures during service conditions exhibits more clearly the loss due to volatility of the antioxidant. This test is a good measure of the long term efficacy of the antioxidant.

More reactive antioxidants give better protection but are also consumed at a faster rate. Hence measurement of residual antioxidant content in blocks after ageing may not give any indication of the efficacy of the antioxidant but it can give an indication of the antioxidant consumption in the tread due to surface oxidation, on the assumption of course that polymer bound antioxidant residues don't give significant antioxidant protection. At least on the wearing surface of the tread, the oxidation zone in which such polymer bound antioxidant residues would be forming is continuously getting worn out and the protection is only given by the antioxidant still retained in the tread. Measurement of loss in % total nitrogen content on truck mounted blocks or blocks subjected to long term ageing at tyre surface temperature during service can give the indication of the physical loss of antioxidant contents by volatilization.

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Vortragstagung „Polymere und Wasser" der GDCh-Fachgruppe Makromolekulare Chemie

Die Fachgruppe Makromolekulare Chemie der Gesellschaft Deutscher Chemiker veranstaltet am 2. und 3. April 1984 in Bad Nauheim ihre turnusmäßige Vortragstagung unter dem Rahmenthema „Polymere und Wasser" mit den Sektionen
I Wasserlösliche Polymere (Synthese, Struktur, Eigenschaften, Anwendungen)
II Polymere Hydrogele (Chromatographie, Medizinische Anwendungen, Enzymfixierung, Polymere Katalysatoren)
III Polymerdispersionen (Emulsions- und Suspensionspolymerisation, Umgekehrte Emulsionspolymerisation, Sekundäremulsion, Mikroemulsion, Kolloidchemie, Rheologische Probleme, Neue Anwendungen, Einkapselung)
Die Anmeldung von Diskussionsvorträgen (15 min Redezeit) bei gleichzeitiger Einsendung einer Kurzfassung von maximal einer DIN A4-Seite wird bis zum 1. Oktober 1983 erbeten an Prof. H. Rudolph, Bayer AG, FE Chemische Forschung, D-5090 Leverkusen. Anmeldung zur Teilnahme bei GDCh-Geschäftsstelle, Abteilung Fachgruppen, Postfach 90 04 40, D-6000 Frankfurt (M.) 90.

IXth International Congress on Rheology

Dieser Kongreß findet vom 8. – 13. Oktober 1984 in Acapulco (Mexiko) statt. Vorträge für diesen Kongreß werden in englischer Sprache erbeten bis 1. Dezember 1983 (Kurzfassung auf einer Schreibmaschine, max. 500 Wörter) an den Sekretär des Organisationskomitees Dr. David M. Binding, IXth International Congress on Rheology, Apdo. Postal 70 – 353, Ciudad Universitaria, Coyoacán, 04510, México, D.F., Mexico.

2.3 Leaching of antioxidants by exposure to water
2.3.1 Exposure of vulcanizate test slabs

Tensile strength test slabs (size: 150 mm x 150 mm x 2 mm) were fixed onto a wooden plank with aluminium foil in between. To prevent the ingress of water behind the test slab from the top and the sides, the aluminium foil was folded over the edges of the test slab to the extent of about 6 mm. All test slabs were fixed in a similar manner in a row over the wooden board and exposed on rooftop of the building facing the southwest both at Kottayam and at Thane for four months (June – September) during the monsoons in 1980. The rainfall at both the places during the exposure period was 2200 mm. After exposure to rains the test slabs were removed and the antioxidant content and the total nitrogen content in the slabs were estimated.

2.3.2 Exposure of vulcanisate blocks

Blocks of 100 mm x 100 mm x 28 mm as used in the block ageing test [9] were covered with aluminium foil with the help of polychloroprene adhesive on five surfaces leaving one 100 mm x 100 mm surface uncovered. These blocks were fitted onto wooden board with the uncovered surface exposed to rains during the period June – October 1982 at Thane and at Kottayam. The rainfall at Kottayam during this period was 1735 mm and at Thane 1975 mm.

To study the leaching effect of continuously running water, standard dumbell test pieces (IS-3400 (Part I), Type I) and blocks as above were used. The dumbells were uncovered. The blocks excepting one 100 mm x 100 mm surface were covered with aluminium foil. The specimen were suspended in a plastic container (separate for each antioxidant vulcanizate). The containers were filled with tap water immersing the test pieces. (Ratio of rubber volume to water volume was about 1:30). Tap water dripped into each container and the rate was adjusted to give one change of water volume per hour. The test pieces were kept immersed for four weeks. The temperature of water remained in the range of $25 - 30\,^\circ\mathrm{C}$ and the pH in the range of $6,5 - 7$. At the end of four weeks the test pieces were taken out and allowed to dry completely for 3 d at room temperature. The dumbell test pieces were then used for determination of tensile strength before and after ageing for 2 d at 100 °C. Antioxidant content and total nitrogen content were determined on the block specimen and only total nitrogen content on dumbells.

2.3.3 Non-extractable antioxidant content

The blocks containing IPPD, ADPA-LV and TMQ after exposure to rains at Kottayam were cut into six layers parallel to the exposed surface, one layer 3 mm from top and the other five all of 5 mm thickness. Acidic solvent extraction was carried out on these slices and nitrogen content on the residue was estimated by Kjeldahl method and from these values the nonextractable antioxidant content was estimated.

2.4 Migration of antioxidants

Blocks 100 mm x 100 mm x 28 mm consisting of two layers of compounds were used. One 14 mm layer consisted of compound with antioxidant and the other 14 mm layer without antioxidant. The interface was very lightly dusted with talcum for ease of separation of the two halves at later stage. The block was cured in the mould at 140 °C in a hydraulic press. The blocks (excepting the set used for the estimation of original antioxidant distribution) were then covered with aluminium foil all around by means of polychloroprene adhesive. The blocks were then kept in the ageing oven at 100 °C for one week and two weeks. The unaged block as also the aged blocks after cooling for 24 h were first separated into two halves. Each half was then sliced into three layers viz. 4 mm, 5 mm and 5 mm thick with the 4 mm layer at the interface; antioxidant content in the slices was then estimated.

2.5 Tyre tests
2.5.1 Antioxidant contents in tyres

The antioxidant contents in the tyre were determined at two points (i) at the crown both on the tread and on carcass and (ii) at the center of sidewall just above the Kerbprotector and on the carcass at this point. The antioxidant content in the carcass was calculated on phr basis on the assumption that it had the same rubber content as in the green calendered fabric used for building the tyre.

For antioxidant migration and consumption studies experimental truck tyres 9.00X20 size lug pattern type were manufactured using only two antioxidants 6PPD and ADPA-LV. The same compound was used for tread and sidewall. Tread/sidewall compound contained 6PPD at 2,5 phr dosage. The carcass compounds contained only ADPA-LV at 1,8 phr dosage. One tyre after moulding was cooled overnight, a quarter section was cut out and the tread/sidewall was separated from carcass in this quarter section. These two parts were then used for antioxidant estimations. The remaining part without separation was stored in cool dark place for about eight months and analysed.

A set of four tyres was sent to Indore region where overloading is prevalent. The tyres were fitted at the rear axle position onto different trucks operated by the commercial truck operators. The tyres were removed from service at definite intervals of tread wear and sections after separation of tread/sidewall from carcass were brought back to the factory and analysed for antioxidant contents.

2.5.2 Abrasion resistance

Abrasion loss was measured as per DIN 53516. The test pieces for laboratory studies were bored from standard test pieces (150 mm x 25 mm x 6,25 mm thick) for De Mattia flex fatigue test (IS-3400 Pt.7). The same De Mattia test pieces were also aged in multicell oven at 70 °C for one, two, four and seven weeks and the abrasion loss after ageing was found on the aged test pieces. For tyre tests the test pieces were bored on the tyre tread at the crown.

2.5.3 Leaching studies

For leaching studies one tyre containing 6PPD from experiment 2.5.1 was used. Another tyre was manufactured with sidewall compound same as above excepting that IPPD content was 2,5 phr. Both the tyres were fitted at rear axle position on a truck plying in Kerala region during both the monsoons (June – February). At the end of the monsoons the tyres were removed from the truck. Both sidewall regions of the tyre were cut out and brought to the factory for antioxidant analysis.

from rubber vulcanizate due to volatility the antioxidant present on the surface (or perhaps in the immediate vicinity of the surface) can get leached out in water due to its solubility in water [3]. As can be seen from the results on blocks leached in running water, the antioxidant in the top layer becomes depleted and is replenished from the interior regions by diffusion. Thus in case of thick articles, the concentration of the antioxidant at the surface will be determined by the concentration of the antioxidant in the bulk and its diffusion characteristics.

Due to depletion of antioxidant from the large surface area and consequent fast reduction in antioxidant level in the bulk, the average loss of antioxidant per unit area of exposed surface during the four month rainy season was far lower in case of thin tensile sheets than in case of the blocks. Table 3 gives the comparison for Kottayam exposed vulcanizates. For want of data on tensile sheets with wax, in case of TMQ and ADPA-HV, the comparison is between sheets without wax and blocks with wax.

Table 3.   Leaching loss per unit area

| Test piece type | 2 mm sheets | | Blocks |
| Antioxidant estimation method | 1[a] | 2[b] | 2[b] |
Antioxidant	Antioxidant loss during 4 months period in g/m²		
IPPD	25,6	–	70,7
6PPD	10,8	–	32,7
77PD	–	0,68	29
TMQ	4,1	–	9,1
ADPA-HV	20,9	–	79,8

[a] From determination of antioxidant content
[b] From determination of total nitrogen content

The antioxidant loss as estimated by the antioxidant estimations includes the antioxidant consumption due to shelf ageing and weathering. For instance the average nonextractable antioxidant content in the IPPD, TMQ and ADPA-HV blocks exposed at Kottayam were 0,68 phr, 0,42 phr and 0,31 phr respectively and can be attributed to the formation of polymerbound or polymeric form of the antioxidant residues nonextractable by solvent. The antioxidant loss as calculated from the loss in total nitrogen content can be regarded as a better indication of loss due to leaching action of water though here also one cannot rule out the possibility of some leaching of the antioxidant residues of the type A-A or A-AH by prolonged contact with water. In case of ADPA-HV only, the difference in the two methods of estimating the loss of antioxidant cannot be fully accounted by the nonextractable antioxidant content. Perhaps the character of at least a part of the antioxidant is changed so as to make it incapable of reaction with the coupling agent without any loss in nitrogen content.

A 900-20 size truck tyre has approximately 1,2 m² of area on tread and sidewall. At a dosage of 2,5 phr in tread and sidewall compounds the antioxidant content in these components will be approximately 320 g. Taking the leaching loss rate as found on the blocks the loss in case of IPPD will be 84,8 g and that in case of 6PPD will be 39,2 g. Such a high difference should be noticeable in field tests.

In order to check the effect of leaching on the ageing characteristics of the vulcanizates, dumbell specimen were subjected to leaching action of running water. To avoid the effects of volatility ageing temperature of 100 °C was se-

lected. Table 4 shows the ageing characteristics before and after leaching in case of the antioxidants IPPD, 6PPD, 77PD, TMQ and ADPA-HV. There was no difference in the unaged physical properties before and after leaching. The ageing test at 100 °C for 2 d did not reveal any significant difference in ageing characteristics except in case of IPPD and ADPA-HV.

Table 4.   Effect of leaching on heat ageing of vulcanisates

| Antioxidant at a dosage of 2,5 phr | Before leaching | After leaching in running water for 4 weeks | |
	% tensile strength retention after ageing 2 d at 100 °C	Antioxidant loss phr[a]	% tensile strength retention after ageing 2 d at 100 °C
IPPD	61	1,59	45
6PPD	57	0,65	56
77PD	68	0,23	66
TMQ	63	0,25	63
ADPA-HV	51	0,69	47

[a] From total nitrogen content determination

3.2 Migration of antioxidants

The temperature at the boundary zone of tread and carcass in the 900-20 size truck tyre under running conditions in India is around 100 °C at the crown reaching as high as 115 °C at the shoulder region. At these high temperatures the interdiffusion of antioxidants from tread to carcass and vice versa can occur at a rapid rate. In order to get a comparative assessment of the rates of migration, a composite block made up of two compounds one with and the other without antioxidant was moulded and then maintained at 100 °C, after covering the block all over with aluminium foil to prevent oxidation. One set was used for estimating the diffusion during moulding process and one set was kept at room temperature for twelve weeks.

Figure 1 shows the extent of migration of antioxidants during the moulding process itself, after twelve weeks storage at room temperature and after one and two weeks at 100 °C. A significant migration occurs in the moulding process itself. After twelve weeks storage at room temperature or after only one week at 100 °C most of the antioxidants had penetrated a thickness of 14 mm and were present on the otherside of the blockhalf without antioxidant. This signifies that during storage of the truck tyre in godown for three months or within less than 10000 km running of the truck tyre, the antioxidant from the tread will have passed through the textile carcass to the inner tube.

The rates of migration of the antioxidants are not equal. The experimental data were found to be not accurate enough and the material accountability as can be seen from Table 5 was far from being satisfactory. The concentration gradient at the interface was not accurately known. Inspite of all these drawbacks diffusion coefficients were calculated from the diffusion curve plotted using the six experimental points and the seventh theoretical point at the interface halfway between the bulk concentrations on both sides of the interface. The equation [12] used was

$$D = \frac{1}{2t} \cdot \frac{dx}{dc} \cdot \int_{c_0}^{c_1} x\,dc$$
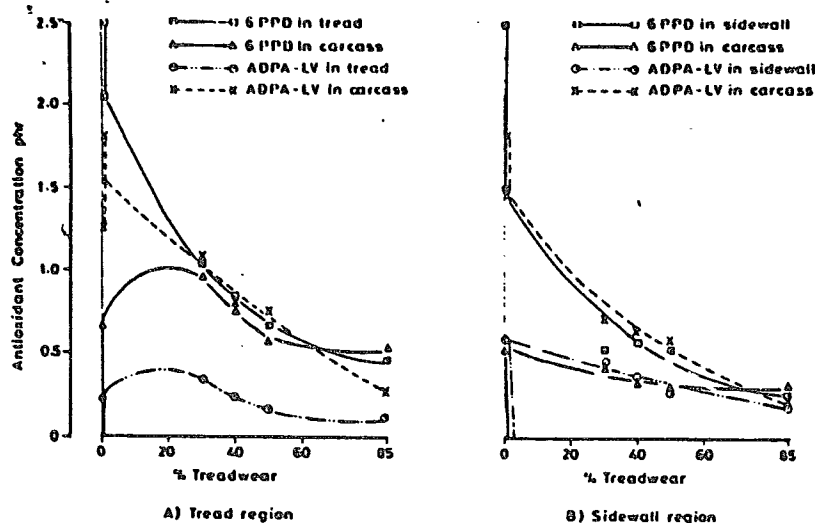
where

Figure 2. Antioxidant concentrations in tyre components; field test of tyres
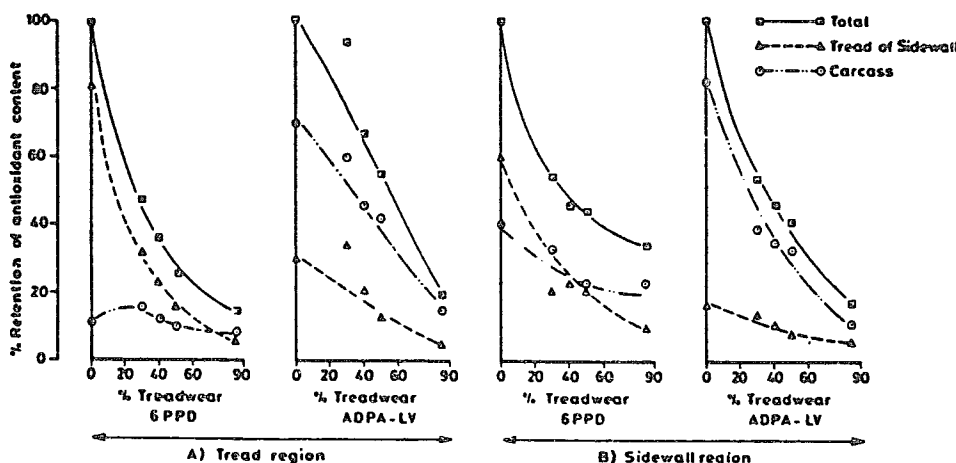

Figure 3. Retention of antioxidant content and distribution in the composite

pounds. The figure also shows the distribution of this retention in the two component parts of the composite.

The migration of the antioxidants must have started at the green tyre stage itself. The high temperatures during the curing operation as also for some time during the cooling down period must have enhanced the migration rate. Hence there was a considerable migration of the antioxidants from the tread and sidewall to the carcass and vice versa in the freshly moulded and cooled truck tyre as can be seen from Figure 2. The tread had lost almost 11 % of its 6PPD contents to the carcass and had gained 30 % of the ADPA-LV contents of the thinner and lower polymer content carcass. Similar situation is also observed on sidewall region where a thin sidewall was in contact with comparative higher polymer content of the carcass. The 6PPD loss from the sidewall to the carcass was almost 40 % of the 6PPD contents of the sidewall while the carcass lost about 17 % of its ADPA-LV contents to the sidewall.

Tread and sidewall of the tyre require protection against ozone and the antiozonants must be present in these components in adequate concentration. Hence to counter the drop in antiozonant concentration due to migration into the carcass Monsanto [6, 8] suggested use of antiozonants in carcass compounds so that the antiozonants from tread/

sidewall do not migrate into the carcass and when the antiozonant concentration at the surface drops to values below those in the carcass, antiozonant from carcass will migrate from carcass to the tread and sidewall surface. This suggestion presumed that no antiozonant consumption occurred on the carcass side and hence the carcass acted as a convenient reservoir for the antiozonants.

As the tyre tread wore down during service, there was a sharp fall in antioxidant concentrations in all the components firstly due to the consumption of the antioxidants while preventing the oxidative degradation of the tyre and secondly due to migration to the neighbouring component. In the tread region the carcass gained in 6PPD concentration in the initial stages and then started losing in concentration of 6PPD. As per the Monsanto concept the flow of 6PPD in the initial stages should have been from tread to carcass but should have reversed in the later stages of tyre life. However, under the Indian conditions of usage of the truck tyre, 6PPD concentration in carcass was for most of the service life of the tyre lower than that in the tread. This fact indicated that almost throughout the life of the tyre 6PPD migrated from tread to the carcass indicating a possibility that there is an oxidative degradation source on the carcass side also consuming the 6PPD migrating from tread side. This aspect will be studied in the next paper.

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dant consumption in the sidewalls will not be of high order and therefore in order to have better differentiation in the results, the tyres were run during both the monsoons (Southwestern monsoons June – October and Northeastern monsoons November – February). At the end of test period tyres were removed from service (treadwear 80 – 85 %) and antioxidant contents in both the sidewall regions of the two tyres were determined. None of the four sidewalls showed any signs of ozone cracking (circumferential cracks). The results of the antioxidant estimations and the % retention of antioxidant contents based on the original quantities added are given in *Table 6.*

Table 6a. Retention of antioxidants after service during monsoons

| | Antioxidant concentration – phr | | | |
	Sidewall		Carcass below sidewall	
Tyre with sidewalls containing 6PPD	6PPD	ADPA-LV	6PPD	ADPA-LV
Sidewall 1	0.63	0.66	0.72	1.18
Sidewall 2	0.49	0.64	0.55	0.87
Tyre with sidewalls containing IPPD	IPPD	ADPA-LV	IPPD	ADPA-LV
Sidewall 1	0.55	0.71	0.56	1.09
Sidewall 2	0.51	0.65	0.52	1.04

Table 6b. % retention of antioxidant contents in the sidewall region

| | Total | of which in | | Total | of which in | |
		side-wall	carcass		side-wall	carcass
	6PPD			ADPA-LV		
Sidewall 1	79	32	47	85	19	66
Sidewall 2	62	20	42	67	18	49
	IPPD			ADPA-LV		
Sidewall 1	65	23	42	82	20	62
Sidewall 2	60	20	40	78	19	59

Contrary to the results expected from the exposure tests on vulcanizate blocks, sidewalls containing IPPD did not show much enhanced loss in antioxidant concentration or contents than the sidewalls containing 6PPD. The inside facing sidewall (sidewall 1) with 6PPD shows higher 6PPD content especially in the carcass than the corresponding sidewall containing IPPD. But the sidewalls facing outside and exposed to rains did not reveal any significant difference between the two antioxidants. As can be seen from distribution of antioxidant contents in Table 6 the reason for the apparent contradiction in experimental results is the rapid diffusion of the PPDs from the thin sidewall to the thick carcass and consequent drop in the PPD concentration levels in the sidewalls very near to the zinc bound antioxidant level. It appears that the zinc bound antioxidant has less tendency to get leached out.

A fact that comes out from the field tests in dry weather in overload conditions and in rainy season with light loads is that the high service temperatures of tyres lead to a far rapid rate of consumption of antioxidants than normal service under wet conditions. The marginal loss of antioxidants due to leaching action of rains is of little consequence in the bias truck tyres with their thick textile carcass bodies.

3.4 Relevance of the studies to steel cord truck radial tyres

Steel cord truck radial tyres have not come to India in significant quantities and no experience is as yet available to us as regards antioxidant performance in these tyres. How-

ever, some projections can be made regarding the usefulness of the present studies for steel cord truck radial tyres.

Overloading is mostly a phenomenon peculiar to the less developed countries and the major damage caused to the truck tyre thereby is the high tyre temperatures during service inspite of the low speeds because of high deflection of the tyre. The steel cord truck tyres, due to their thin single ply carcass body are expected to run comparatively cooler than the bias ply tyres under same service conditions. However, in developed countries due to better condition of the roads the sustained speeds are higher in the range of 80 – 90 km/h and the duration of continuous run is also longer. These service conditions can lead to development of high temperatures in the body and on the surface of the tyre tread and volatile loss of antioxidants can still take place. The antioxidant consumption rate may also be as high as that observed in the case of bias tyres.

In the bias tyres migration of the antiozonants into the carcass brings down the antiozonant concentration in tread and sidewalls to low values, but because of this very reason, leaching loss of the antiozonant from the tyre does not become significant. In steel cord truck radial tyre, due to the comparatively small quantity of rubber in the carcass, migration of antiozonant into the carcass will have insignificant effect on the concentration of the antiozonant in the tread or in the sidewall, but due to the consequent high concentration levels of antiozonant present in these components leaching action of water can lead to significant losses of antiozonants as also of certain amine antioxidants.

In the bias tyres, the antioxidant content in the carcass stocks are also available to certain extent for the protection of the tread and sidewalls by migration phenomenon. If high temperature service conditions are expected for steel cord radial truck tyre it will be necessary to use comparatively higher dosages of antioxidants in the tread and sidewall compounds than in case of the corresponding bias tyre compounds to compensate for the antioxidant coming from carcass of the bias ply tyre and to give prolonged protection during the longer wear life expected of the radial tyre.

4. Summary

In bias ply truck tyres, migration of antioxidants from tread and sidewalls to the carcass and vice versa occurs during the manufacturing operations and continues during storage and service life of the tyre.

Significant loss of certain amine antioxidants occurs from vulcanizate blocks due to the leaching action of the rains. Due to rapid diffusion into the thick textile carcass and consequent low concentrations on the surface of the sidewalls, loss of antiozonants from the sidewalls due to leaching action of rain is not very significant.

Due to the extensive cross migration of the antioxidants in the tyre during production and during service life, addition of function-specific antioxidant to the separate component compounds of the truck tyre has little relevance in the service life of the truck tyre. What will matter is the total antioxidant quantity present in the specific region e.g. the tread region composed of the tread and the carcass below the tread or the sidewall region composed of the sidewall and the carcass below the sidewall.

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ОКР

INFLUENCE OF VOLATILITY OF SOME P-PHENYLENE-DIAMINE DERIVATIVES ON EFFICIENCY OF THEIR STABILIZING ACTION IN THERMOOXIDATIVE AGEING OF CKII-3-BASED TIRE RUBBER COMPOUNDS

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Systems of stabilizers widely used for protecting tread and sidewall compounds against fatigue and ozone contain, as a rule, the blend of a p-phenylenediamine derivative (usually it is N-isopropyl-N'-phenyl-p-phenylenediamine) and a derivative of dihydroquinoline (for example, 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline).

As is known,/1-4/ the derivatives of p-phenylenediamine (PPDA) are effective antiflexing agents and antiozonants, and their introduction into rubber compounds increases considerably the time before fatigue and ozone cracks appear.

Dihydroquinoline derivatives (DHQ), for example, quinol ED and Acetonesnyl P, used in blends with PPDA reduce considerably the rate of ozone crack growth. A blend of PPDA and DHQ provides sufficient protection of tread and sidewall compounds against cracking. However, some data are available /5-6/ that long before the end of service the concentration of stabilizers decreases considerably. Obviously, this is primarily a result of physical loss, i.e. volatilisation at elevated temperatures and washing-out in contact with a wet road.

Taking into account differences in service conditions and deformation cycles of various tyre elements, it seemed interesting

tion.

The data on the absence of a change in the stress relaxation rate for samples containing built-in PNDPA during the whole period under consideration indicate that the main means for stabilizer consumption is volatilization.

The stress relaxation rate constant for a vulcanizate containing PNDPA does not increase that testifies to non-significant chemical consumption (for reactions of oxidation chain scission and air oxygen) of built-in PNDPA at 130°C during the experiment for 90 minutes.

Taking into account the chemical affinity of built-in PNDPA and PPDA under investigation, the same indirect conclusion may be drawn in relation to other derivatives of PPDA, except DMP which is capable, as was already mentioned, of being consumed in the reaction with air oxygen.

Thus, an increase in the stress relaxation rate constant of vulcanizates containing stabilizers of PPDA is due primarily to stabilizer volatilization.

Another proof that the main cause of PPDA derivative consumption in the vulcanizates studied is volatilization, is presented by data on a reduction in the concentration of these stabilizers during sample heating in an inert gas medium when "chemical" stabilizer consumption is minimum. These experiments conducted in a nitrogen flow showed that as to the volatilization rate the PPDA under investigation rank in the same order, i.e. the decisive factor in the decrease of vulcanizate concentration in the air is also volatilization rather than participation in the reactions of oxidation chain scission or direct oxidation by air oxygen.

An important role played by the volatilization of PPDA deriva-

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Desc, the delay in stress relaxation after stabilizer addition in the initial stages (up to 30 - 50 min), further on the process of relaxation is accelerated. Relaxation rate constants determined 70-90 minutes after the beginning of the process for samples containing stabilizers are close to the rate constant for non-stabilized samples.

In contrast to this, vulcanizates with a built-in PNDPA do not exhibit an increase in the relaxation rate. One may assume that the most likely reason for accelerating the stress relaxation in vulcanizates stabilized by PPDA is a reduction in the content of stabilizers during relaxation due to volatilization and other mechanisms of reducing their concentration.

From the data of Fig.3 on the kinetics of changing the stabilizer concentration in samples after heating, in a relaxometer at 130°C a conclusion may be drawn that for all the low-mass PPDA a monotonic concentration reduction is observed. The highest rate of a concentration change at this temperature was found for N,N'-di (1,3-dimethylbutyl)-p-phenylenediamine (DMP), while the lowest one for N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (DMBP). ... is an intermediate one.

Taking into account the fact that the rate of cleavage of N1- and mode change of rubber oxidation during thermooxidative degradation depends slightly on the structure of substituents in the aromatic ... stage of stabilizers of PPDA /14-15/. the difference in the rate of consumption of ... stabilizers may be ascribed primarily to non-effective loss for the above ... .

Besides, one would take into consideration a higher reactivity of dialyl derivatives of PPDA as compared to arylalkyl and diaryl derivatives /16/ in the reactions of direct oxidation with air oxygen that may be an additional reason for rapid DMP consump-

Table 2

Change in Tensile strength and Stabilizer Content during Tread and Sidewall vulcanizate Ageing

Stabiliser	Ageing time hrs at 100°C	Ageing coefficient in relation to tensile strength	Stabilizer content % from control sample
no stabiliser	24	0.65	—
no stabiliser	48	0.57	—
no stabiliser	72	0.36	—
N,N'-di(1,4-dimethyl-pentyl)-p-phenylenediamine (DMP)	24	0.69	traces
	48	0.52	traces
	72	0.35	traces
N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD)	24	0.68	12.6
	48	0.59	4.4
	72	0.35	1.9
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (MBPP)	24	0.67	33.2
	48	0.60	19.9
	72	0.38	3.4

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ELASTOMER MECHANICS WITH ACCOUNT FOR STRUCTURE ELEMENTS

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An expression for specific free energy [1,2] has been derived on the basis of the thermodynamics of non-equilibrium processes, using the CLAUSIUS-DUGHEM inequality and a microscopic model of flexible-chain elastomers with a macronetwork structure, and thermoelastoplastics. For large elastomer strains and small but finite viscoelastic strains of the nodes of a spatial macronetwork, stress-strain relationships have been obtained. The physical meaning and restrictions for relaxation constants and functions have been established and a method for their determination suggested.

1. Relaxation Properties and Structure of Elastomer Spatial Macronetwork

An elastomer spatial macronetwork consists of polyfunctional groups (nodes) of microheterogeneous inner structure, and free portions of macromolecular chains that connect these groups [3]. Thus, spatial macronetwork groups in thermoelastoplastics, such as butadiene-styrene and isoprene-styrene blockpolymers, are microparticles of glassy polystyrene, 180-300 Å in size.

When rubber is vulcanized with acryl compounds (magnesium and zinc methacrylates), the spatial macronetwork groups are represented by salt crystallites in the form of 140-300 Å microphase particles resulting from salt polymerisation. Network groups of similar structure are obtained from vulcanization with polyacryl esters of glycols and polyesters, and maleic and vinyl compounds.
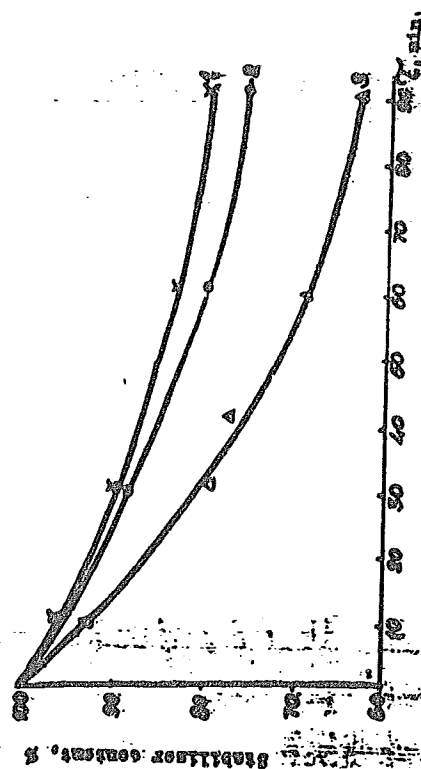

Fig.3. Kinetics of stabilizer volatilization from CKMC-3 based gum vulcanisates (130°C, air)

1 - N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine   Zonfler
2 - N-isopropyl-N'-phenyl-p-phenylenediamine   Iped
3 - N,N'-di-(1,4-dimethyl-pentyl)-p-phenylenediamine   Vofler 2,
diamine.